Thermally stable electrical contacts to GaN

Lars Voss[1], L. Stafford[1], J.S. Wright[1], R. Khanna[1], S.J. Pearton[1], H.T. Wang[2], J.J. Chen[2], and F. Ren[2]

[1]Department of Materials Science and Engineering, University of Florida, Gainesville, FL, USA, 32611

[2]Department of Chemical Engineering, University of Florida, Gainesville, FL, USA 32611

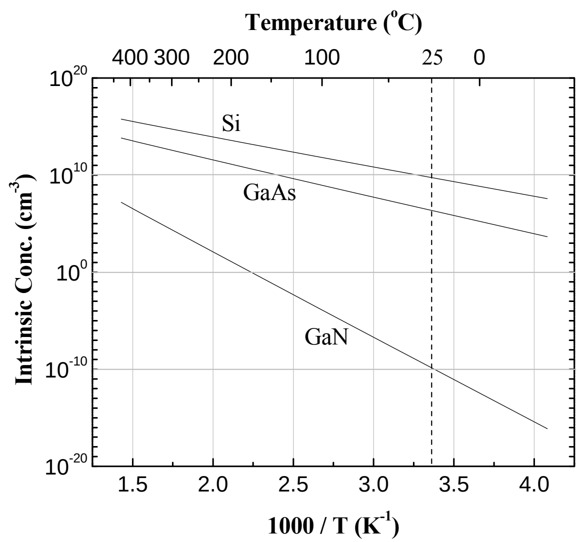
Outline

- Introduction
  - GaN
- Experiments
  - n-GaN Ohmic contacts
  - p-GaN Ohmics contacts
- Conclusion

Introduction to GaN: Electronic Properties

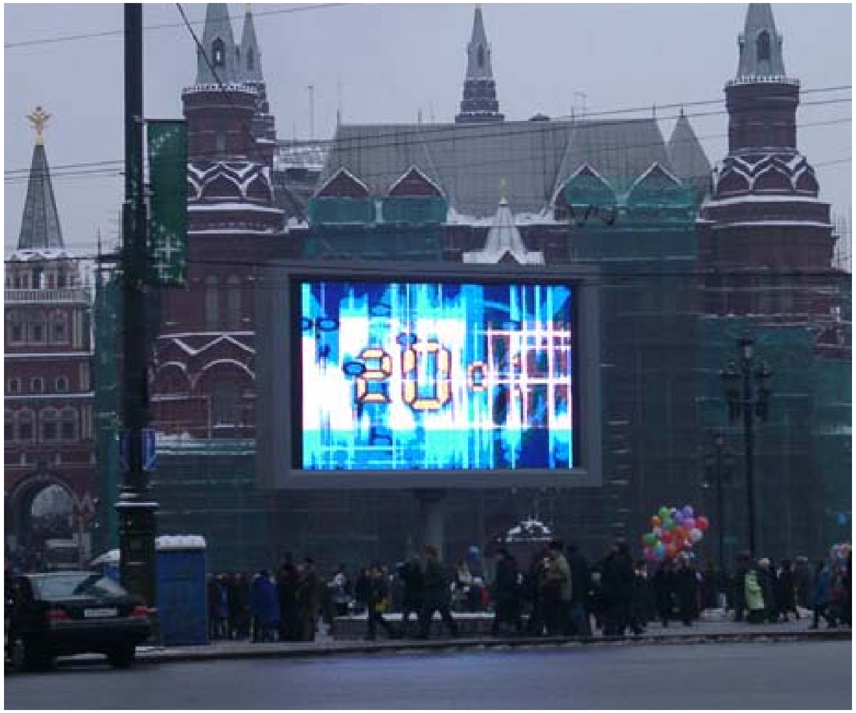
- III-V Semiconductor
- Intriguing properties
  - Direct, wide band gap
  - Low intrinsic carrier concentration
  - High breakdown field
  - High electron mobility and saturation velocity
  - Good thermal conductivity

	Si	GaAs	GaN	AlN	6H-SiC
Bandgap (eV) @ 300 °C	1.1 Indir.	1.4 direct	3.4 direct	6.2 direct	2.9 indirect
Electron mobility ($cm^2/V\cdot s$), RT	1400	8500	1000 (bulk) 2000 (2D-gas)	135	600
Hole Mobility ($cm^2/V\cdot s$), RT	600	400	30	14	40
Saturation velocity (cm/s), 10^7	1	2	2.5	1.4	2
Breakdown field (V/cm), $x10^6$	0.3	0.4	>5		4
Thermal conductivity (W/cm)	1.5	0.5	1.5	2	5
Melting temperature (K)	1690	1510	>1700	3000	>2100



Introduction to GaN: Potential Applications

- Ultraviolet light emitter
  - Use of alloys with In and Al for tunable emission (1.92-6.2 eV)
- High power, high temperature electronics
  - HEMT and MMIC devices
  - Applications in nuclear reactors, high temperature fuel cells, and outer space



Nitride properties

- Nitrides appear promising
  - High melting points
  - Large work functions
  - Desirable thermal and electrical conductivities
  - Studied for a variety of applications

Properties	TaN	TiN	ZrN
Melting point (K)	3633	3203	3253
Structure	FCC	FCC	FCC
Thermal expansion coefficients x 10^6 (/deg)	3.6	9.4	8.7
Work function (eV)	4.7	3.74	4.6
Lattice constant (Å)	4.3	4.32	4.574
Thermal conductivity (W m^{-1} K^{-1})	57.5	19.2	20
Electrical resistivity (μΩ-cm)	15.52	25	13.6

Boride properties

- Family of borides appears to be very promising
  - High melting points
  - Large work functions
  - Desirable thermal and electrical conductivities
  - Used to resist corrosion by molten metals indicates low solid solubilities

Properties	TiB_2	ZrB_2	W_2B	W_2B_5	CrB_2
Melting Point (°C)	2980 ~3225	3040 ~3200	~2670	~2385	2200
Structure	hexagonal	hexagonal	-	hexagonal	hexagonal
Thermal expansion coefficients x 10^6 (/deg)	4.6	5.9	-	-	10.5
Phonon component of heat conduction (wt/m-deg.)	20.6	18.9	-	-	10.4
Elastic modulus E x 10^{-6} (kg/cm^2)	5.6	4.3	-	-	2.5
Characteristic Temperature (°K)	1100	765	-	-	726
Density of electronic states g x 10^{-21} (eV^{-1} cm^{-1})	4.50	4.76	-	-	54.6
Work function (eV) (approx.)	4.19(?)	3.94(?)	-	-	3.18(?)
Heat of Formation (Kcal/mole)	71.4	76.0	-	-	31.0
Lattice constant(A)	3.028	3.169	-	2.982	2.969
Thermal conductivity(W.m^{-1}$_K$$^{-1}$)	26	80	-	unknown	32
Electrical resistivity(μOhm.cm)	28	4.6	-	19	21

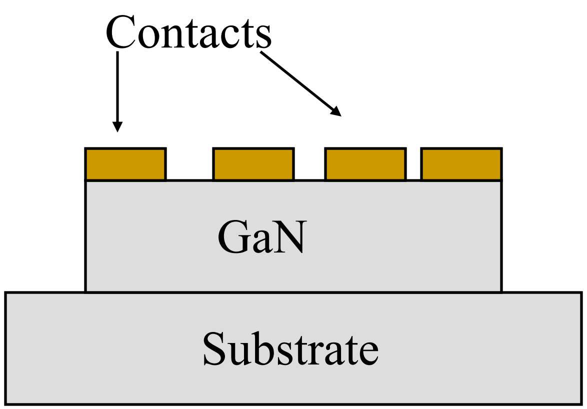
Iridium properties

Properties	Ir
Melting point (K)	2719
Structure	FCC
Thermal expansion coefficients x 10^6 (/deg)	6.4
Work function (eV)	5.27
Lattice constant (Å)	3.8
Thermal conductivity (W m^{-1} K^{-1})	147
Electrical resistivity (μΩ-cm)	4.71

- Ir may be promising for contacts
  - High melting point
  - Large work function
  - Desirable thermal and electrical conductivities
  - No Ir-N phases at processing temperatures

Experiments: Ohmic contact processing

- Acetone and IPA rinse
- Photolithography
- Mesa etch
- KOH dip (p-GaN only)
- Photolithography
- O_2 plasma descum
- $HCl:H_2O$ dip
- Sputter metal deposition
- Lift off
- 300-1000C anneals



Ohmic to n-GaN background

- Requirements
  - Comparable contact resistance to conventional schemes
  - Good stability as a function of anneal temperature, time, and during aging
  - Minimize intermixing of layers
    - Formation of viscous $AlAu_4$ is detrimental

→

- Approach
  - Replace diffusion barrier metals with nitride materials
    - Should act as a better diffusion barrier at high temperatures than metals
    - Reduces intermixing of layers
    - Do not expect resistance to be adversely affected

Previous work with borides to n-GaN

- Recent work also showed improved stability for boride-based Ohmic contacts for hydrogen sensing

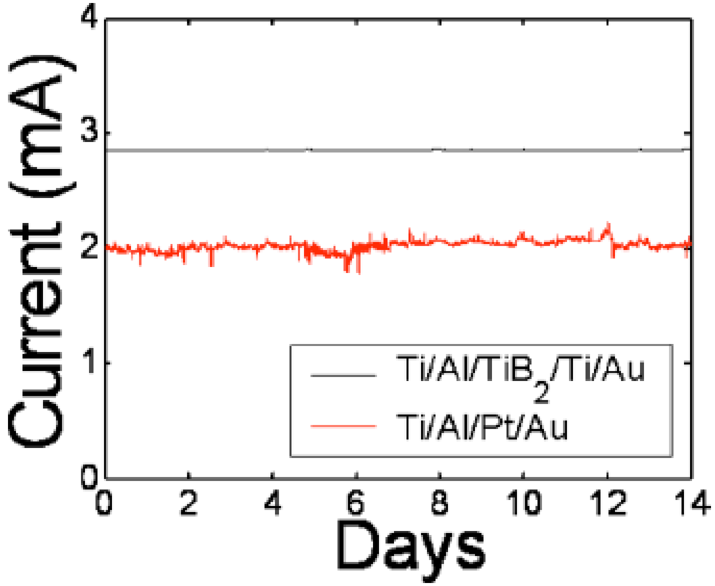
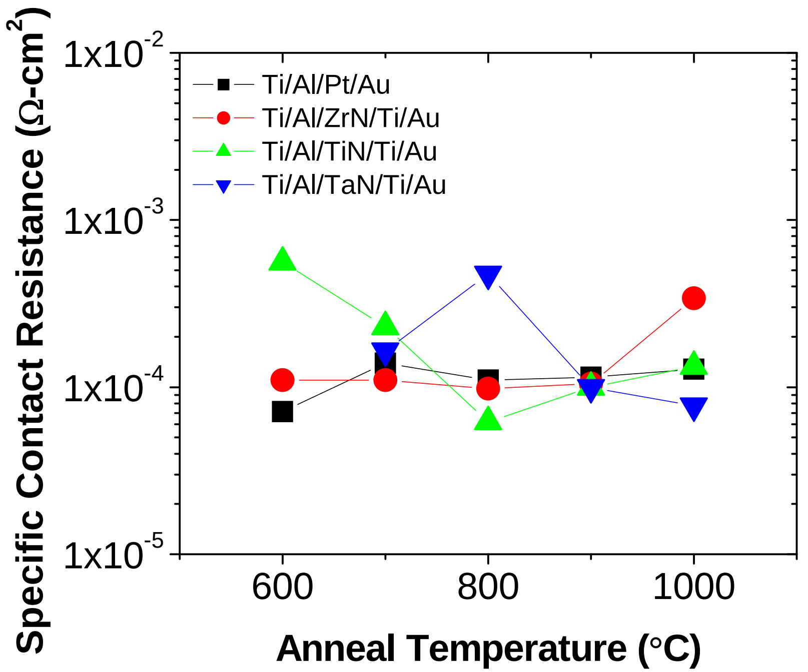


FIG. 4. (Color online) Variation in forward current at fixed bias for diodes with boride-based Ohmic contacts (top) or conventional Ohmic contacts (bottom) as a function of time under field conditions where the temperature increases during the day and decreases at night.

Wang et al., "Stable hydrogen sensors from AlGaN/GaN heterostructure diodes with TiB_2-based Ohmic contacts", Appl. Phys. Lett. 90, 252109 (2007).

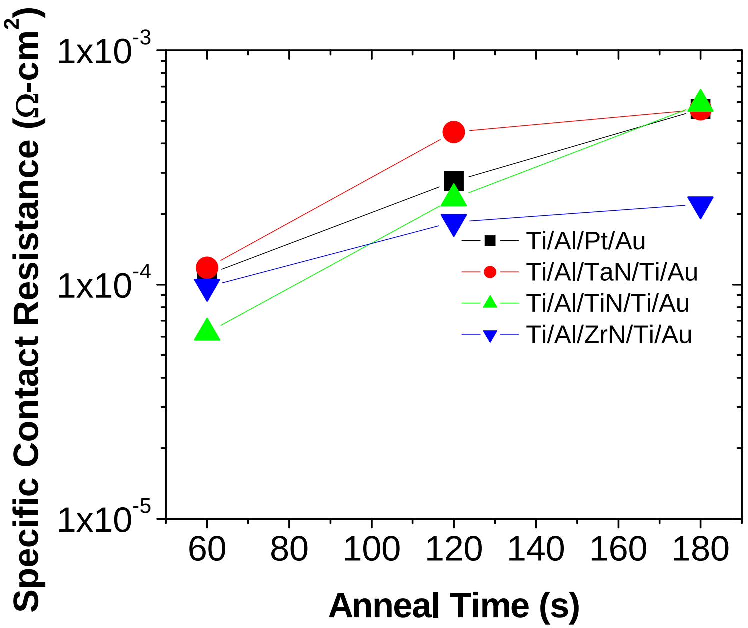
Ohmic contacts to n-GaN

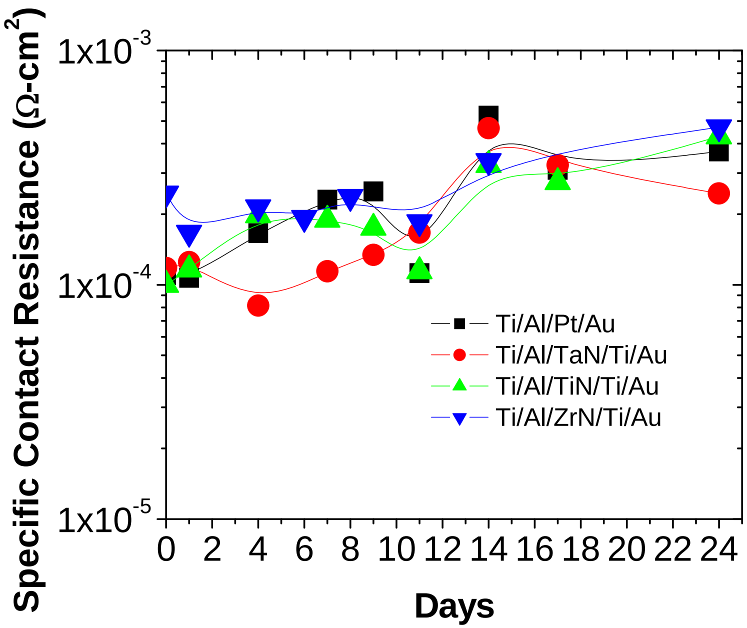
- Samples doped at ~3 x 10^{17} cm^{-3}
- Ti/Al/X/Ti/Au
  - X is TaN, TiN, or ZrN
  - Ti overlayer necessary for Au adhesion to nitride
  - Au to reduce sheet resistance



- Anneals in flowing N_2 ambient

Stability characteristics



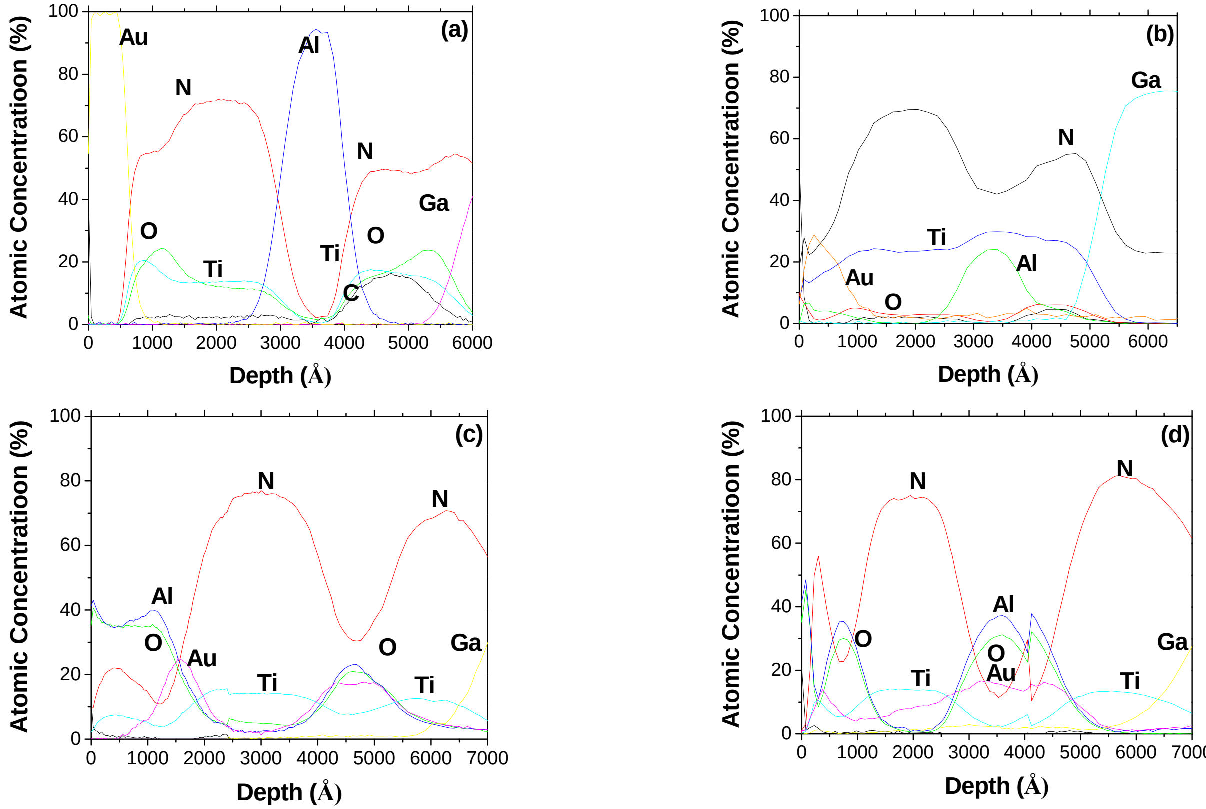


Contact	Percent Change
Ti/Al/Pt/Au	236%
Ti/Al/TaN/Ti/Au	107%
Ti/Al/TiN/Ti/Au	330%
Ti/Al/ZrN/Ti/Au	91%

AES for n-GaN (TiN-based)

As dep

600°C



800°C

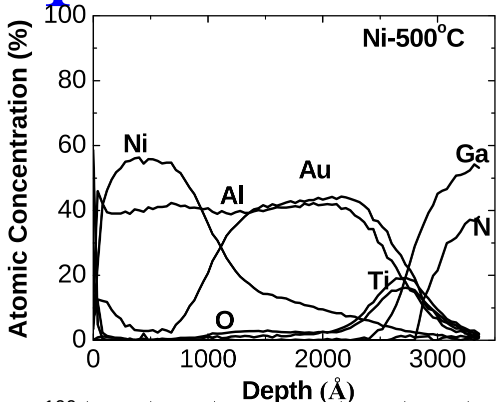
800°C aged

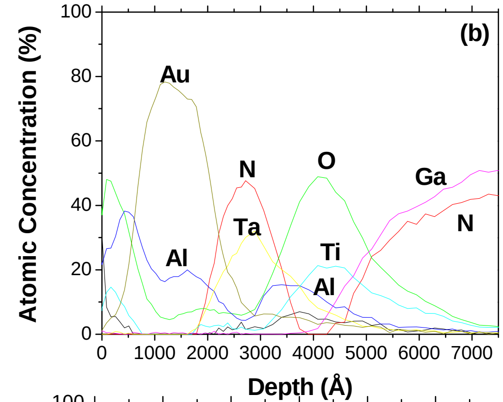
- Similar profiles for all three nitrides
- Contacts maintain somewhat layered structure
- Aging at 350°C appears to have no effect

Comparison to Ti/Al/Ni/Au

Ni

500°C



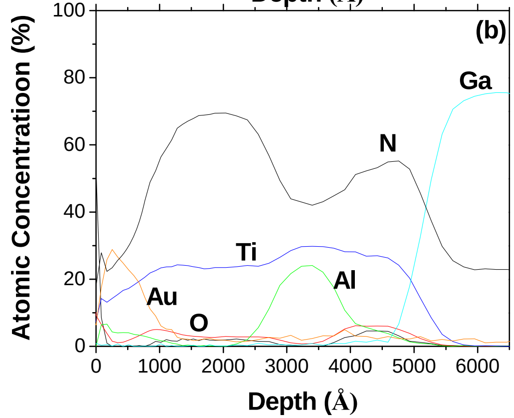


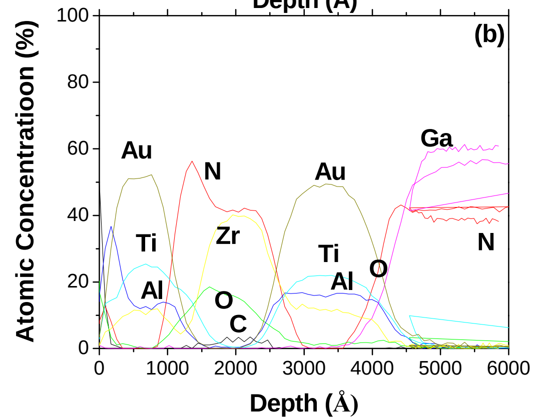
TaN

600°C

TiN

600°C





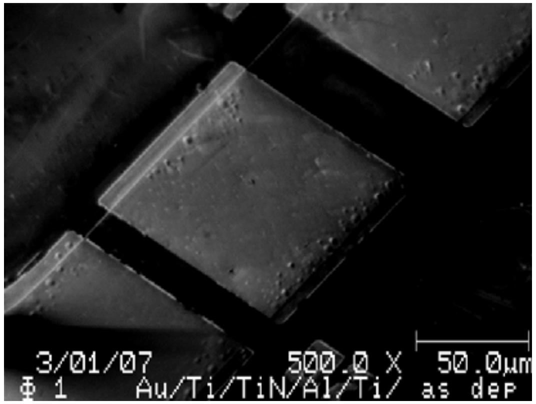
ZrN

600°C

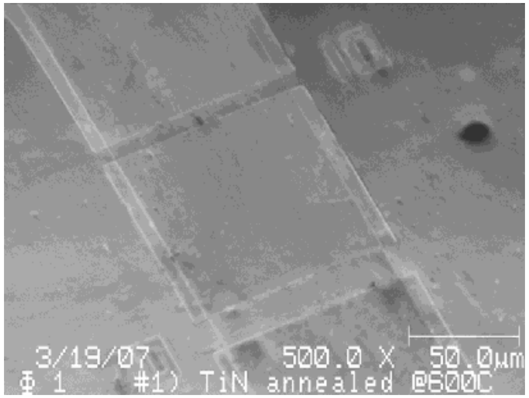
- Compared to Ni diffusion barrier, nitride based contacts show far superior depth profiles with minimal intermixing

Materials Science & Engineering

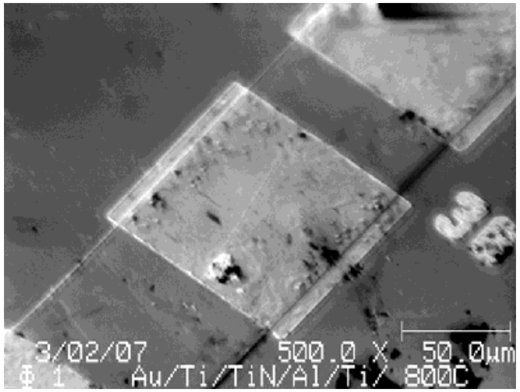
SEMs for n-GaN (TiN-based)



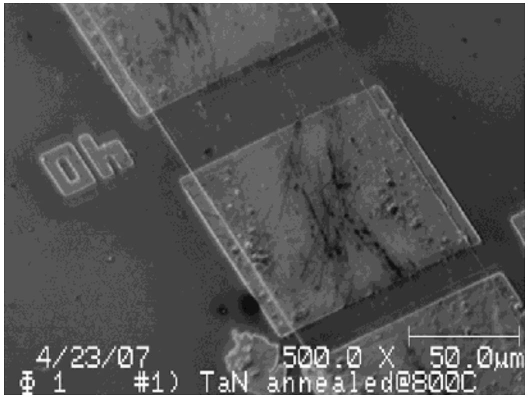
As deposited



600 ^{o}C anneal



800 ^{o}C anneal

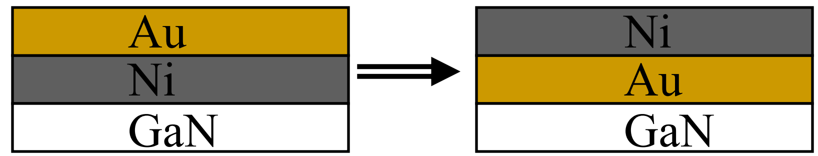


800 ^{o}C anneal, aged

Ohmic contacts to p-GaN background

- Requirements
  - Low contact resistance
  - Thermally stable
  - Minimize intermixing of layers
- Current schemes
  - High workfunction metal such as Ni, Pd, Pt, Cr with an overlayer of Au
  - Ni/Au contacts ~ 10^{-4} ohm-cm^2 are most common

Ni/Au



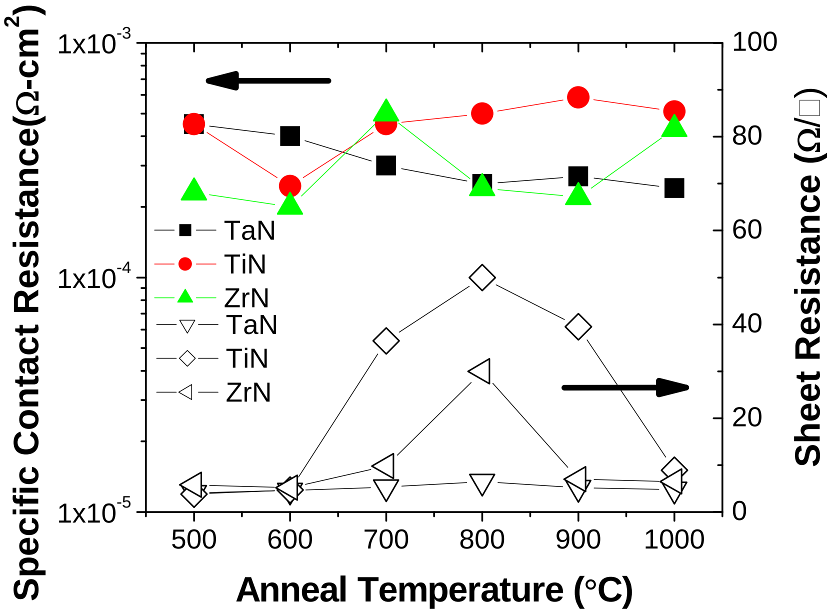
- >400^{o}C anneals
- Rough Ni surface
- Poor thermal stability
- Ni/Au is still the best scheme
  - Ni removes H from Mg-H complexes
  - Au forms Au-Ga intermediate phases at 600^{o}C

Ohmic contacts to p-GaN

- Why does it transform?
  - Lower energy configuration
  - Omiya et al. suggests it is due to preferential bonding
  - Electronegativities
    - Au – 2.4
    - Ni – 1.6
    - Ga – 1.5
  - Ni-Au phase diagram also shows a miscibility gap
- Approach
  - Utilize high temperature barrier to delay this configuration
    - TiN, TaN, ZrN
      - Ti – 1.5
      - Ta – 1.5
      - Zr – 1.33
  - Also allows for an overlayer for a smoother morphology
    - GaN/Ni/Au/X/Ti/Au

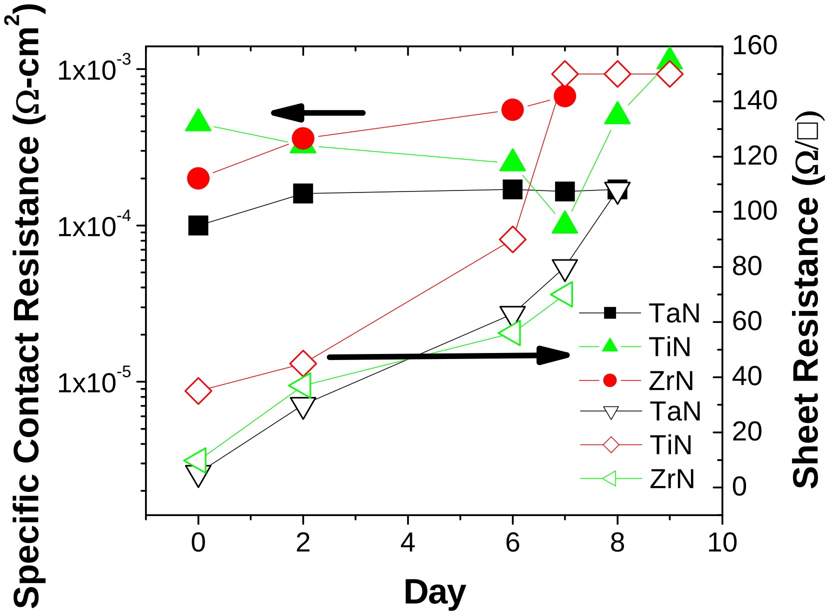
Appl. Phys. Lett. 85, 6143 (2004).

Nitride based Ohmic contacts to p-GaN



- Specific contact resistance is stable over a wide range of anneal temperatures
  - Onset of Ohmic behavior corresponds to temperatures at which Au-Ga phases have been observed
- Spike in sheet resistance
  - Due to increased in-diffusion without complete alloying?

Long term aging for nitrides to p-GaN



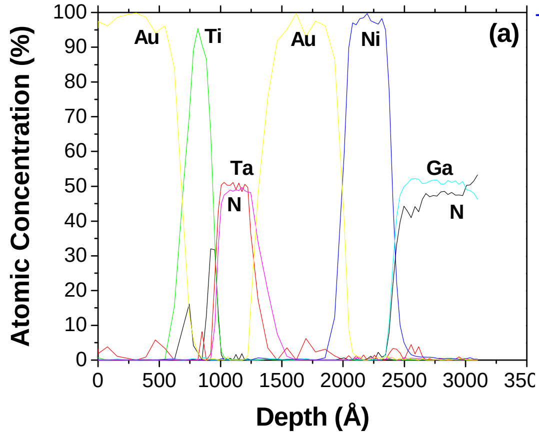
- Contacts are no longer Ohmic after ~ 9 days at 200°C
- Sheet resistance consistently increases
  - Due to increased in-diffusion to GaN of Ti, Zr, or Ta
    - Atoms may be interstitials
    - Exchange between Ga and Ti/Zr/Ta may produce a decrease in Gibb's free energy due to increased entropy

- Gibb's Free Energy of Formation

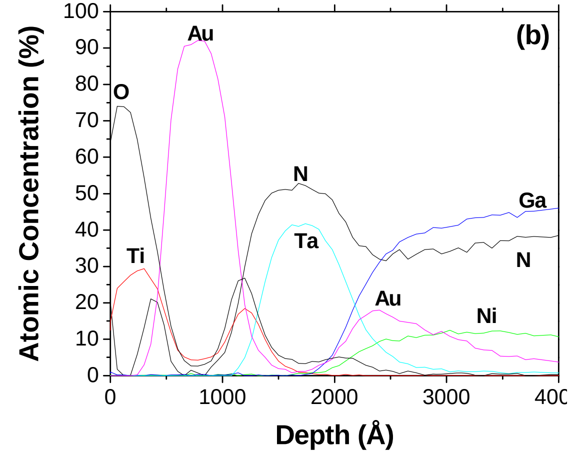
$$\Delta_f G^o = \Delta_f H^o - T\Delta_f S^o$$

AES for TaN to p-GaN

As dep



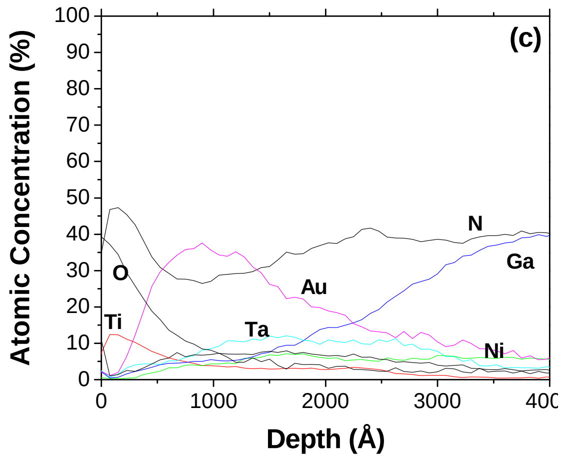
600 °C



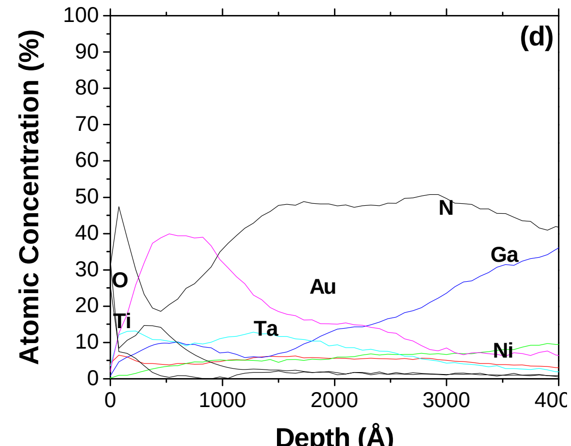
700°C

+

Aged

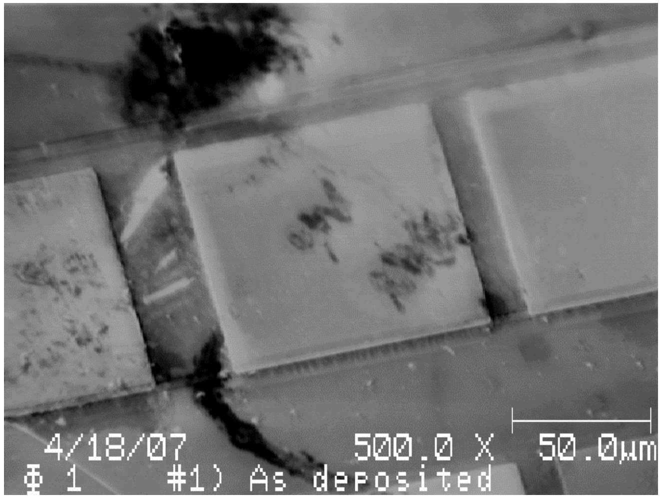


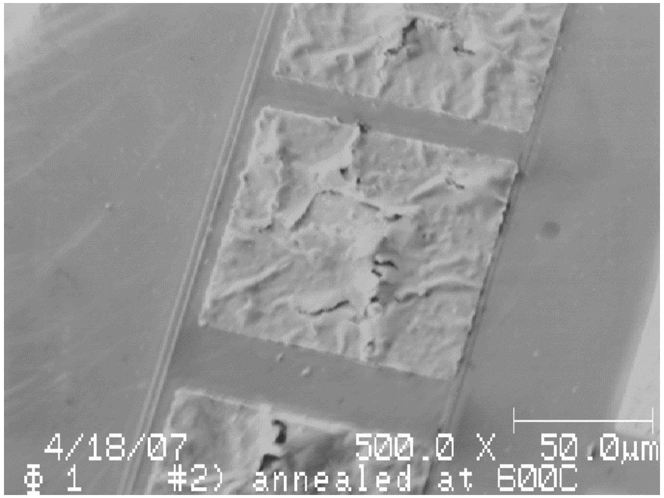
1000 °C

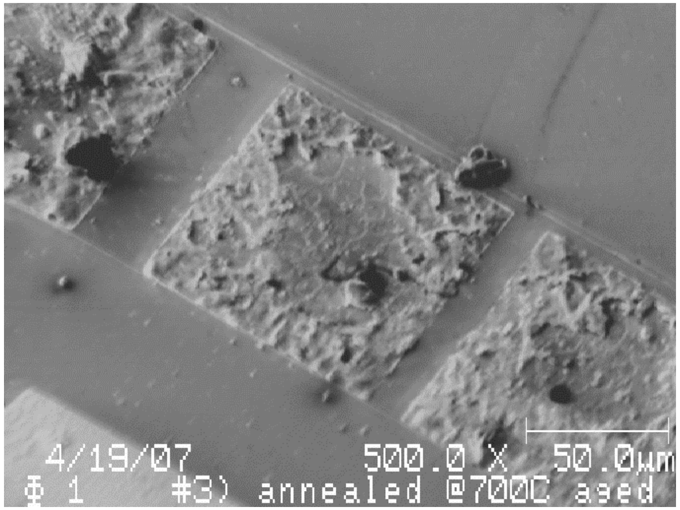


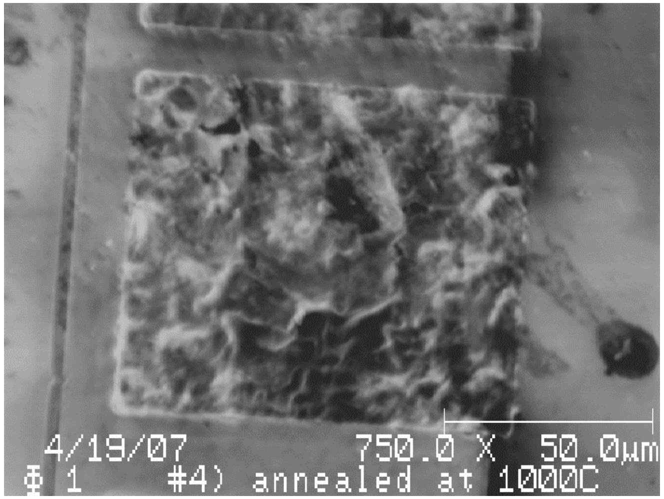
- At 600°C, diffusion of Au and Ni into GaN
- Aged contacts show a breakdown of the nitride

SEMs for TaN to p-GaN

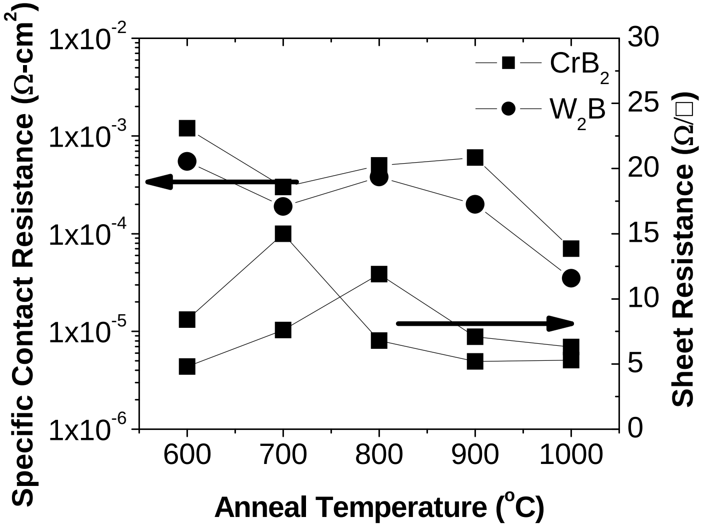


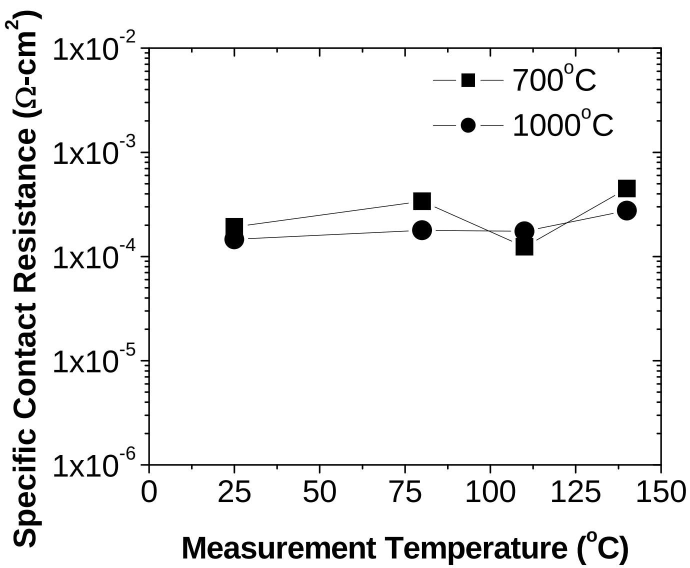






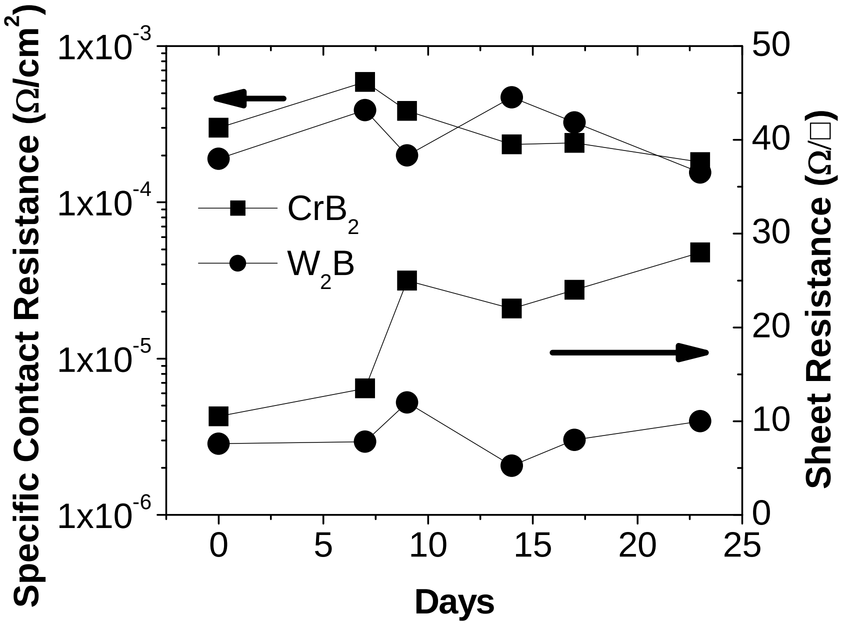
Boride based Ohmic contacts to p-GaN





- Specific contact resistance is stable over a wide range of anneal temperatures
  - Onset of Ohmic behavior corresponds to temperatures at which Au-Ga phases have been observed
- Sheet resistance fairly stable
  - Indicates stability of contacts on p-GaN
- Independent of measurement temperature
  - Transport by tunneling

Long term aging for p-GaN



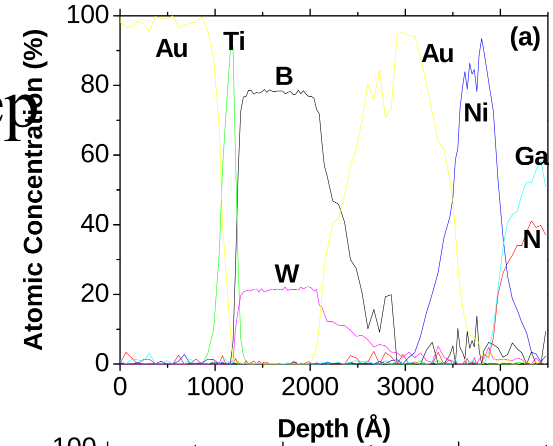
- Contacts remain Ohmic after >20 days at 350^{o}C
- Sheet resistance is consistent
  - CrB_2 may show increase due to low heat of formation
    - Little interaction between GaN and borides
    - No evidence that Ga-B phases exist
    - Large change in Gibbs Free Energy prevents reactions

- Gibb's Free Energy of Formation

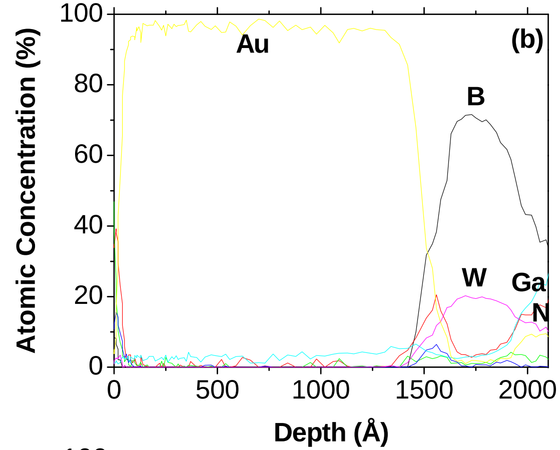
$$\Delta_f G^o = \Delta_f H^o - T\Delta_f S^o$$

AES for W_2B to p-GaN

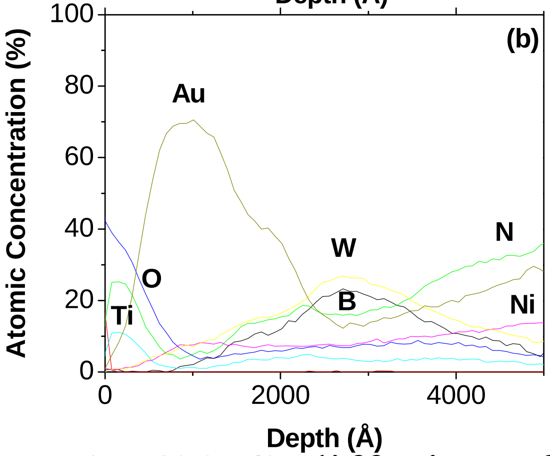
As dep



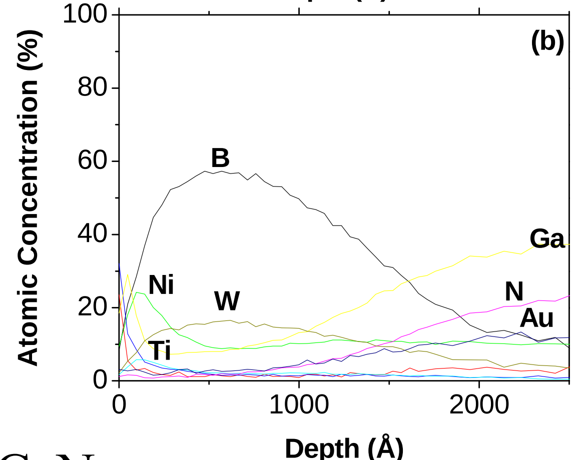
600 °C



700°C + Aged

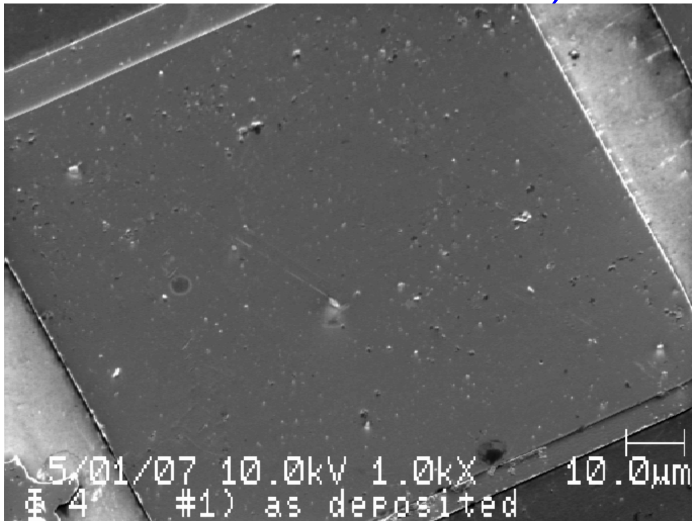


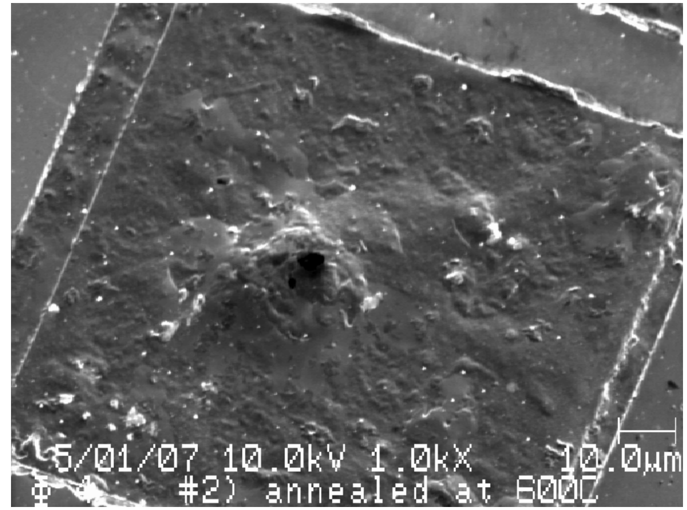
1000 °C

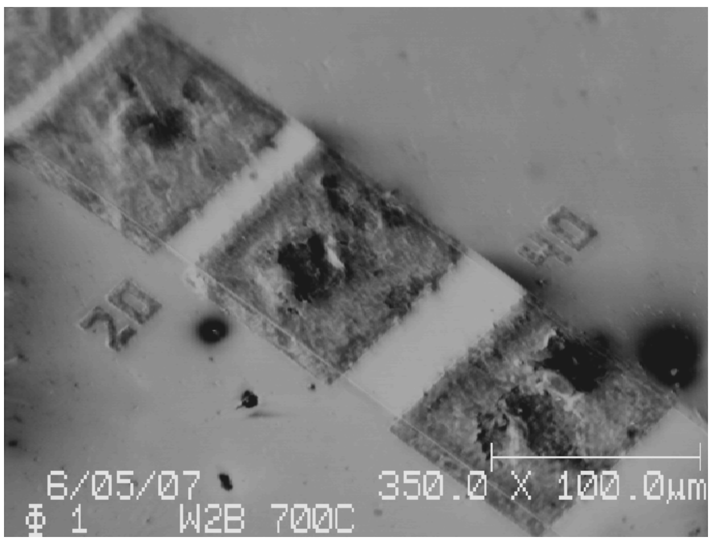


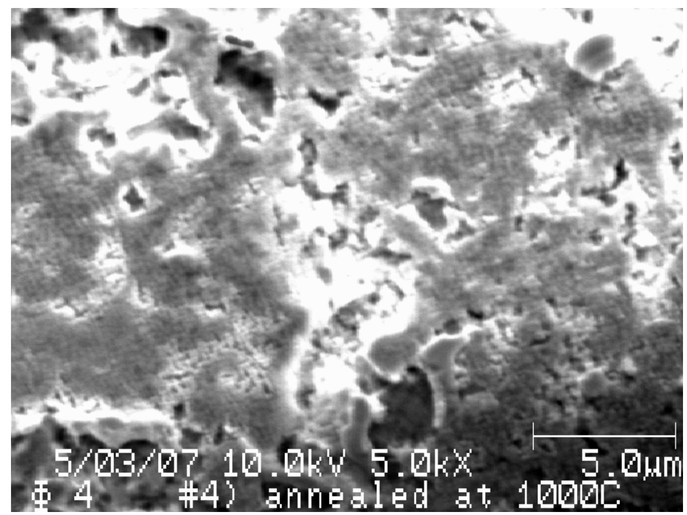
- At 600°C, diffusion of Au and Ni into GaN
- Aged contacts show some diffusion of boride, but no breakdown is evident

SEMs for W_2B to p-GaN

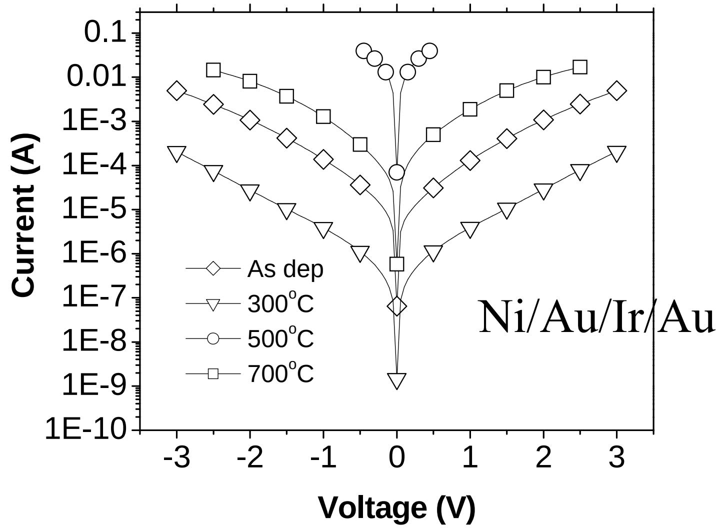


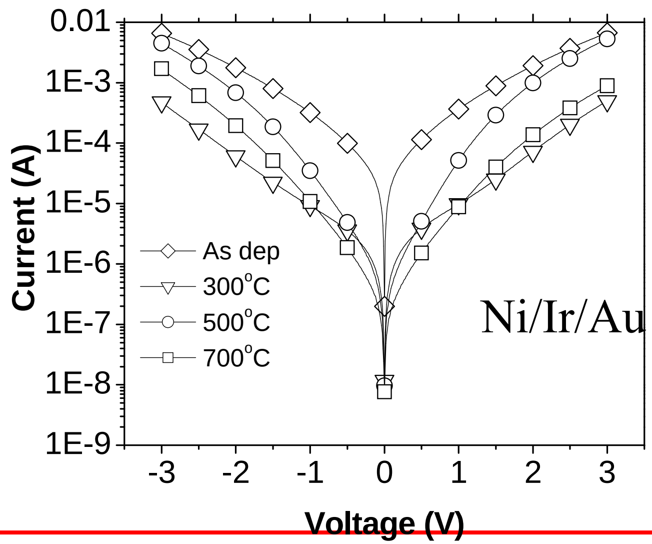






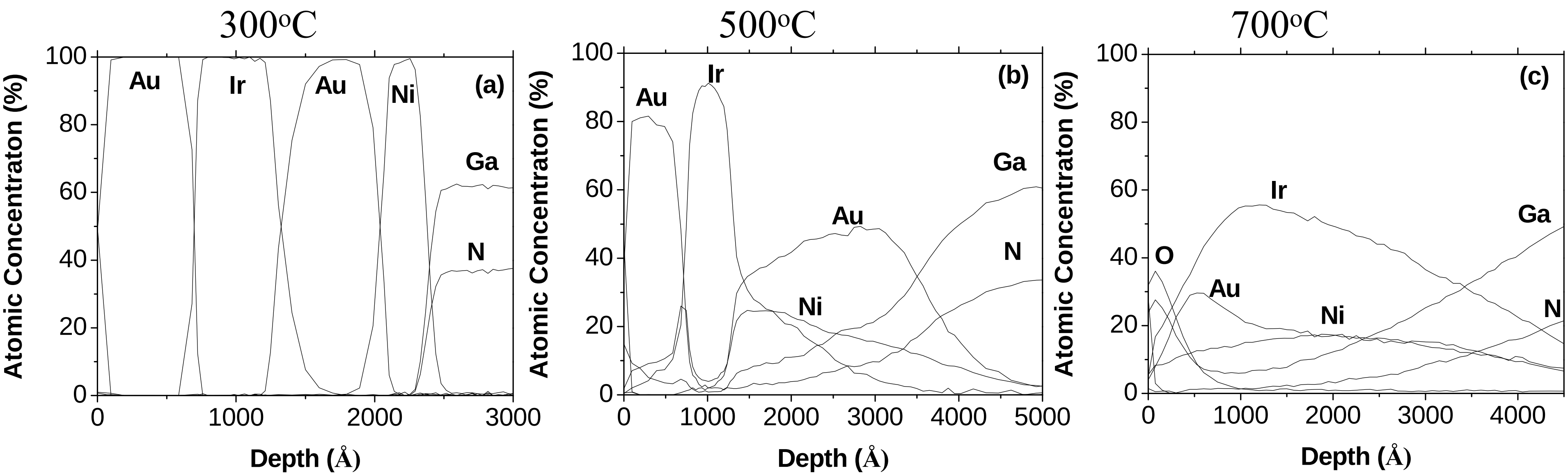
Ir-based Ohmic contacts to p-GaN





- Only GaN//Ni/Au/Ir/Au displays Ohmic behavior
  - Only at 500°C anneal
  - Initial decrease in current at 300°C likely due to Ir in-diffusion to GaN
  - Demonstrates importance of Au on surface
  - Ni/Ir/Au displays a slight increase in current at 500°C, likely due to removal of H by Ni

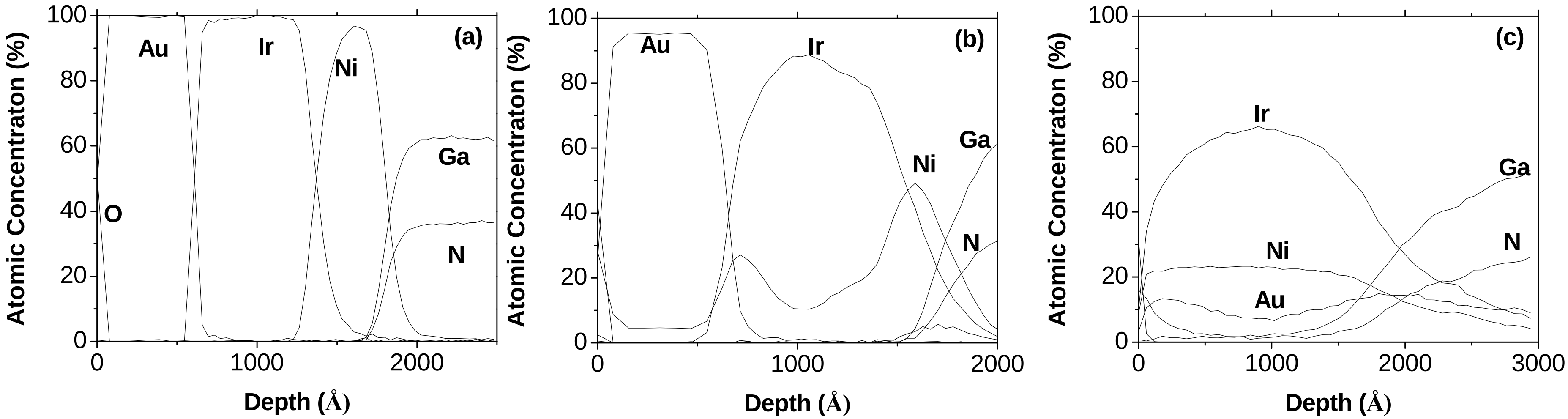
AES Ni/Au/Ir/Au to p-GaN



- Layer structure intact at 300°C => little reaction at surface
- At 500°C, Au has likely reacted with Ga to increase the surface doping
- At 700°C, diffusion of Ir into GaN disrupts transport
  - No Ir-N phases exist at these conditions

AES Ni//Ir/Au to p-GaN

300°C 500 °C 700 °C



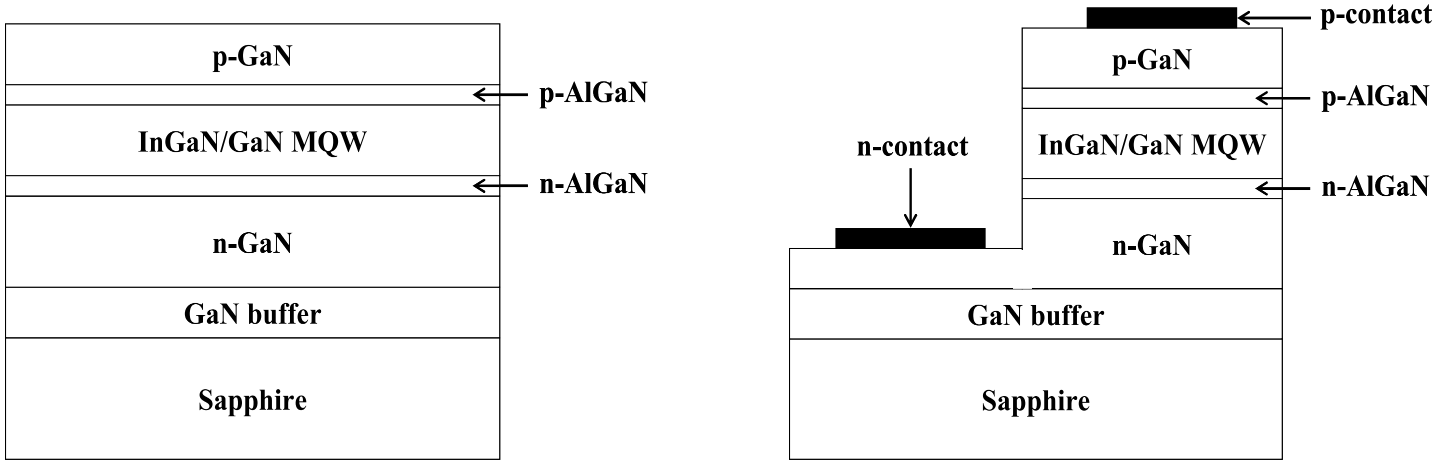
- Layer structure intact at 300°C => little reaction at surface
- Increases in anneal temperature result in increased diffusion of Ir to GaN, resulting in increased scattering events which correspond with decreased current

Summary of Ohmic results

Contact Scheme	$\rho_{sc,minium}$ (Ω-cm^2)	Anneal temperature (^oC)	Failure temperature (^oC)
Ni/Au/W_2B/Ti/Au	3.5×10^{-5}	1000	>1000
W_2B/Ti/Au	1.69×10^{-3}	800	>900
Ni/Au/CrB_2/Ti/Au	7×10^{-5}	1000	>1000
Ni/Au/TiB_2/Ti/Au	1.93×10^{-4}	850	>900
Ni/Au/ZrB_2/Ti/Au	1×10^{-4}	900	>900
ZrB_2/Ti/Au	1.8×10^{-3}	800	>900
Ni/Au/TaN/Ti/Au	2.5×10^{-4}	800	>1000
Ni/Au/TiN/Ti/Au	2.45×10^{-4}	600	>1000
Ni/Au/ZrN/Ti/Au	2×10^{-4}	600	>1000
Ni/Au/Ir/Au	2.3×10^{-4}	500	>500
TaN/Ti/Au	3.7×10^{-4}	800	>1000
ZrN/Ti/Au	3.1×10^{-4}	600	>700

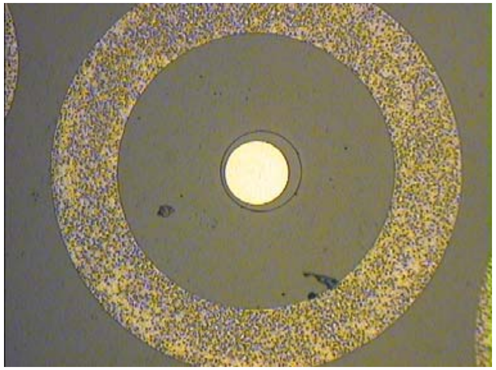
- Some Ohmic behavior present with nitrides/borides directly on surface with no Ni/Au layer, but generally poor and not available over a wide range of temperatures
- Very high failure temperatures

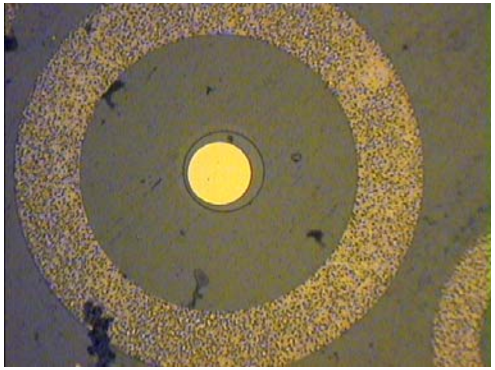
MQW LEDs with Ir and TiB_2

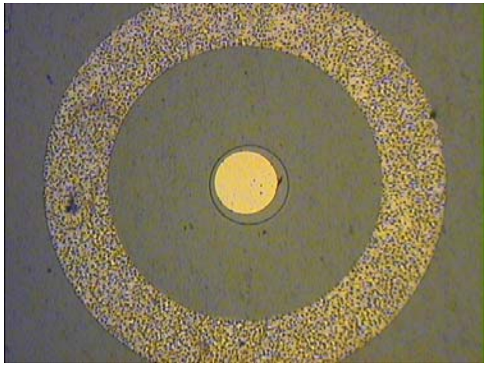


- Processing
  - Contacts patterned by photolithography / lift-off
  - Mesa Etch (~1µm) in ICP (Cl_2/Ar plasma) for the n-Ohmics
  - n-Ohmics: e-beam deposited Ti/Al/Pt/Au annealed at 800°C for 60s
  - p-Ohmics: sputter-deposited metals
    - Ni(50 nm)/Au(80 nm)/**boride**(50 nm)/Ti(20 nm)/Au(80 nm)
    - Ni(50 nm)/Au(80 nm)/**Ir** (50 nm)/Au (80 nm)

Morphology of LEDs


Ni/Au

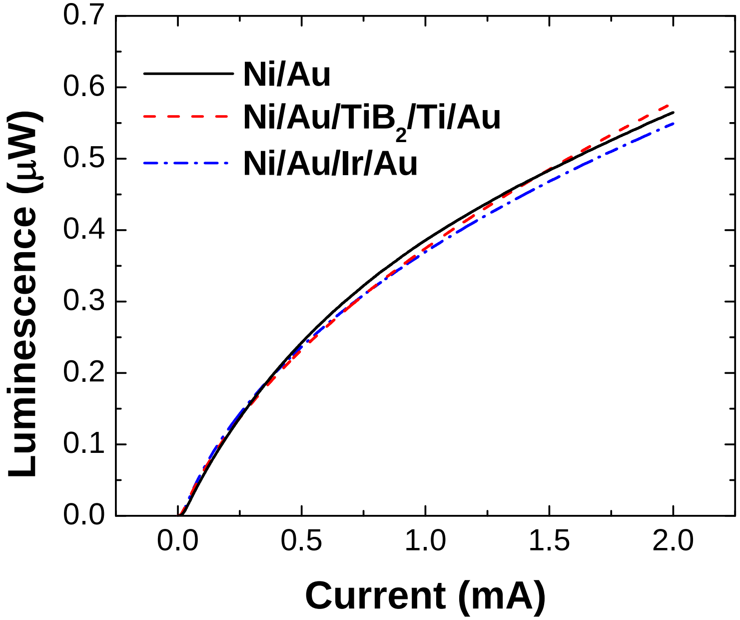

Ni/Au/TiB_2/Ti/Au


Ni/Au/Ir/Au

- All metallizations display similar morphologies

MQW-LED characteristics

- L-I characteristics (output power measured using a Si photodetector located at ~2 cm from the sample surface)

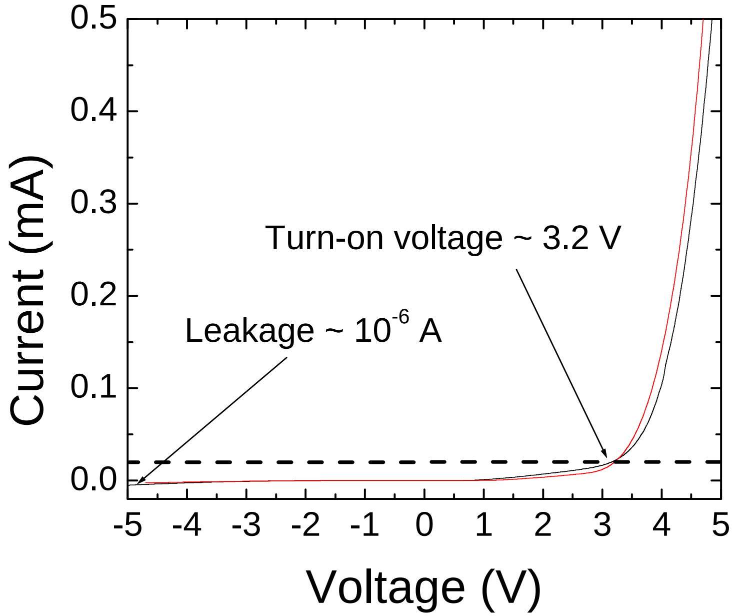


- Similar L-I for all metallization schemes, showing that the TiB_2/Ti/Au or Ir/Au overlayers did not reduce the light output with respect to Ni/Au contacts
- Non-linear increase and relatively low output power can probably be attributed to self-heating effects

Guo et al., Appl. Phys. Lett. 78, 3337 (2001)
Chitnis et al., Appl. Phys. Lett. 81, 3491 (2002)

MQW-LED characteristics

- I-V characteristics

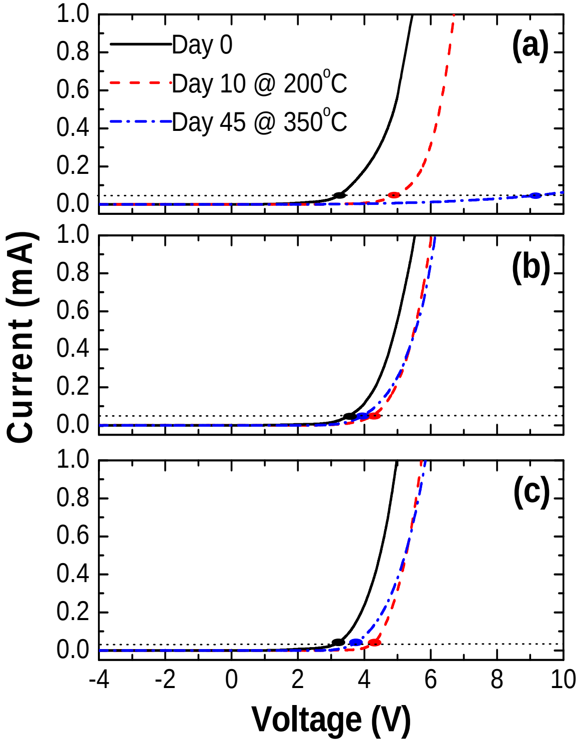


- For all diodes, the ideality factor was >2, consistent with previous studies reported in literature
- For all as-fabricated devices, the turn-on voltage was 3.1-3.4V and the reverse leakage current was $\sim 10^{-6}$ A
- Such high leakage currents are commonly observed in GaN-based LEDs grown on sapphire and result from the high density of dislocations in such samples

X.A. Cao et al., Appl. Phys. Lett. 85, 7 (2004).

MQW-LED characteristics

- Influence of long-term annealing on the I-V characteristics



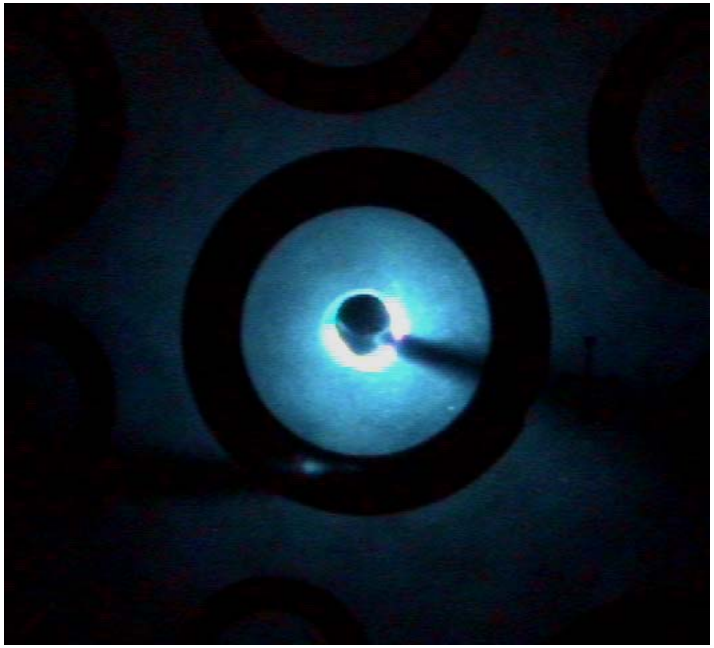
- 10 days aging at 200ºC
  (i) Increase of the turn-on voltage
  (ii) Decrease of the leakage current

- Extra 30 days aging at 350ºC
  (i) TiB_2- and Ir-based devices show turn-on voltage and leakage current similar to those in the as-deposited state
  (ii) serious degradation in LEDs fabricated with Ni/Au contacts

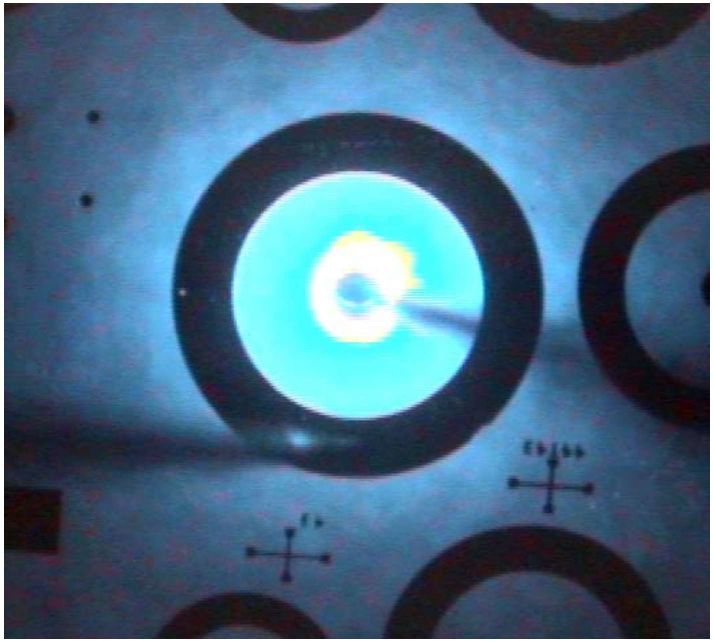
Contact to p-GaN	Turn-on voltage (V)			Reverse current @ -5V (A)		
	Day 0	Day 10 200°C	Day 45 350°C	Day 0	Day 10 200°C	Day 45 350°C
Ni/Au	3.3±0.3	4.9±0.4	9.1±0.5	$(2\pm1)\times10^{-6}$	$(6\pm2)\times10^{-9}$	$(5\pm3)\times10^{-5}$
Ni/Au/TiB2/Ti/Au	3.4±0.2	4.1±0.5	4.0±0.2	$(5\pm2)\times10^{-6}$	$(2\pm1)\times10^{-9}$	$(2\pm1)\times10^{-8}$
Ni/Au/Ir/Au	3.3±0.2	4.3±0.3	3.9±0.3	$(3\pm1)\times10^{-6}$	$(2\pm1)\times10^{-9}$	$(3\pm2)\times10^{-7}$

MQW-LED characteristics

- Impact of degradation on output power



Ni/Au -- 80 uA @10V



Ni/Au/TiB_2/Ti/Au -- 300 uA @ 4.5V

Reduction of injected current at a given forward voltage had a large impact on the EL output

Schottky to p-GaN: Previous results

- Variety of barrier heights reported on p-GaN
  - 0.5~2.9 eV even for the same metals
- Use of borides on n-GaN
  - Low barrier heights 0.6~0.8 eV
- Borides as ohmic contacts
  - Provide good diffusion barrier in Ni/Au/XB/Ti/Au on p-type ohmic contacts
  - Suggests minimal interaction of borides with metals as well as GaN

Conclusions

n-GaN

- Specific contact resistance is stable over a wide range of anneal temperatures
- Comparable contact resistance to conventional contacts
- Decreased layer mixing compared to Ni diffusion barriers

p-GaN

- Increased anneal temperatures possible for nitrides and borides
- Borides and Ir display excellent stability under long term thermal aging

Acknowledgements

The work at UF was partially supported by AFOSR grant under grant number F49620-03-1-0370, by the Army Research Office under grant no. DAAD19-01-1-0603 and the National Science Foundation (DMR 0400416, Dr. L. Hess).